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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1995	3. REPORT TYPE AND DATES COVERED Abstract presented April 2-7, 1995	
4. TITLE AND SUBTITLE Processes Affecting Nitro Reduction by Iron Metal: Mineralogical Consequences of Precipitation in Aqueous Carbonate Environments			5. FUNDING NUMBERS N/A	
6. AUTHOR(S) Abinash Agrawal, P.G. Tratnyek, P. Stoffyn-Egli, and L. Liang				
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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) SERDP 901 North Stuart St. Suite 303 Arlington, VA 22203			10. SPONSORING / MONITORING AGENCY REPORT NUMBER N/A	
11. SUPPLEMENTARY NOTES Abstract presented from the American Chemical Society Division of Environmental Chemistry at the 209th ACS National Meeting, Vol.35(1), Anaheim, California, pp. 720-723, 2-7 April 1995. This work was supported in part by SERDP. The United States Government has a royalty-free license throughout the world in all copyrightable material contained herein. All other rights are reserved by the copyright owner.				
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13. ABSTRACT (Maximum 200 Words) In aqueous systems, zero-valent iron metal is readily oxidized by many substances to ferrous iron. These reactions may be considered as corrosion processes in which oxidation of Fe^0 to Fe^{2+} is the anodic half-reaction. In anoxic pure aqueous media the only available cathodic half-reactions involve H^+ and H_2O as electron acceptors (oxidants). Rapid corrosion requires more favorable cathodic reactions, of which the reduction of dissolved O_2 is certainly the most important. However, other electron acceptors offer additional cathodic reactions that can contribute to iron corrosion. Possible oxidants of primary interest in groundwater remediation include anthropogenic contaminants such as chlorinated solvents, nitro aromatic compounds, and chromate. In addition, most contaminated waters contain substantial amounts of secondary solutes that are also oxidants relative to iron metal and, therefore, must be considered in any process-level interpretation of field performance. Among these solutes, carbonate is certainly one of the most important.				
14. SUBJECT TERMS SERDP, zero-valent, corrosion, aromatic compounds				15. NUMBER OF PAGES 4
				16. PRICE CODE N/A
17. SECURITY CLASSIFICATION OF REPORT Unclass.	18. SECURITY CLASSIFICATION OF THIS PAGE Unclass.	19. SECURITY CLASSIFICATION OF ABSTRACT Unclass.	20. LIMITATION OF ABSTRACT UL	

"PREPRINTED EXTENDED ABSTRACT"

Presented Before the Division of Environmental Chemistry
 American Chemical Society
 Anaheim, CA April 2-7, 1995

PROCESSES AFFECTING NITRO REDUCTION BY IRON METAL:
 MINERALOGICAL CONSEQUENCES OF PRECIPITATION
 IN AQUEOUS CARBONATE ENVIRONMENTS

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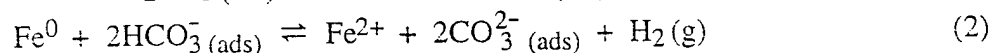
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In aqueous systems, zero-valent iron metal is readily oxidized by many substances to ferrous iron. These reactions may be considered as corrosion processes in which oxidation of Fe⁰ to Fe²⁺ is the anodic half-reaction. In anoxic pure aqueous media the only available cathodic half-reactions involve H⁺ and H₂O as electron acceptors (oxidants). Rapid corrosion requires more favorable cathodic reactions, of which the reduction of dissolved O₂ is certainly the most important. However, other electron acceptors offer additional cathodic reactions that can contribute to iron corrosion. Possible oxidants of primary interest in groundwater remediation include anthropogenic contaminants such as chlorinated solvents, nitro aromatic compounds, and chromate. In addition, most contaminated waters contain substantial amounts of secondary solutes that are also oxidants relative to iron metal and, therefore, must be considered in any process-level interpretation of field performance. Among these solutes, carbonate is certainly one of the most important.

Carbonate may effect metal corrosion in several ways. The acceleration of metal corrosion by dissolved CO₂ is well-established largely due to studies of corrosion in the anaerobic, carbonate-rich condensates that occur during oil and gas production. This phenomenon involves adsorbed H₂CO₃ and HCO₃⁻ species that react as oxidants to drive metal dissolution [1].



Equilibration with water restores the original carbonate speciation, so the net result of equations 1 and 2 is catalysis of H₂ evolution by corrosion of iron mediated with carbonate. Decreased corrosion rates are expected when carbonate precipitation forms a protective layer on the metal surface, as it frequently does in water distribution systems [2]. Similar behavior may occur where iron is used in an effort to remediate contaminated groundwater. Although formation of FeCO₃ is

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thermodynamically favored under conditions of environmental interest (Fig. 1), the kinetics of this reaction are generally slow, so the effect of carbonates on contaminant reduction by iron is likely to vary with temporal as well as chemical conditions.

In our investigations of nitro reduction by Fe^0 [3], we have gained insight into the effects of carbonate by using an aqueous model system buffered with CO_2 . Batch experiments were performed in anaerobic bicarbonate buffer medium ($\text{Carbonate}_{\text{Total}} = 1.5 \times 10^{-2} \text{ M}$) using 33.3 g/L Fluka iron turnings (18-20 mesh, specific surface area = $0.02 \text{ m}^2/\text{g}$) and nitrobenzene as an organic oxidant. Preliminary handling of the Fe^0 and mixing rate during the experiments were carefully controlled.

First-order rate constants for nitro reduction, k_{obs} , were obtained routinely and provided our first evidence for interactions between Fe^0 and carbonate (Figs. 2-3). Values of k_{obs} declined with increased carbonate concentration (Fig. 2) and with extended exposure of the metal to a particular carbonate buffer (Fig. 3). The appearance of a gray precipitate in these batch studies (long after the nitro reduction experiments were complete) suggested that formation of microcrystalline carbonate mineral phases at the metal surface may be occurring throughout the reaction time of our experiments.

The effect of carbonate precipitation at the metal surface is being further investigated by Scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS). SEM of clean iron samples (Fig. 4 a-b), and those subsequently exposed to aqueous bicarbonate medium (Figure 4 c-d), has revealed the formation of a non-uniform layer on the metal surface consisting of crystalline aggregates. EDS analysis has confirmed that these aggregates are predominantly iron carbonates (FeCO_3). The formation of FeCO_3 (s) on the metal surface occurred only in bicarbonate medium, and was not observed on metal surfaces exposed to deoxygenated water for equal duration. One important variable that remains to be investigated is the effect of mixing (and, in particular, abrasion) on the development of the FeCO_3 surface film.

It can be concluded that the observed decrease in nitro reduction rate is due to accumulation of non-reactive iron carbonate aggregates that inhibit mass-transfer of reactants and products to and/or from the reactive sites on the metal surface. Further characterization of metal surface evolution in the presence of natural groundwater solutes will be necessary to reliably predict the field performance of remediation installations involving iron metal.

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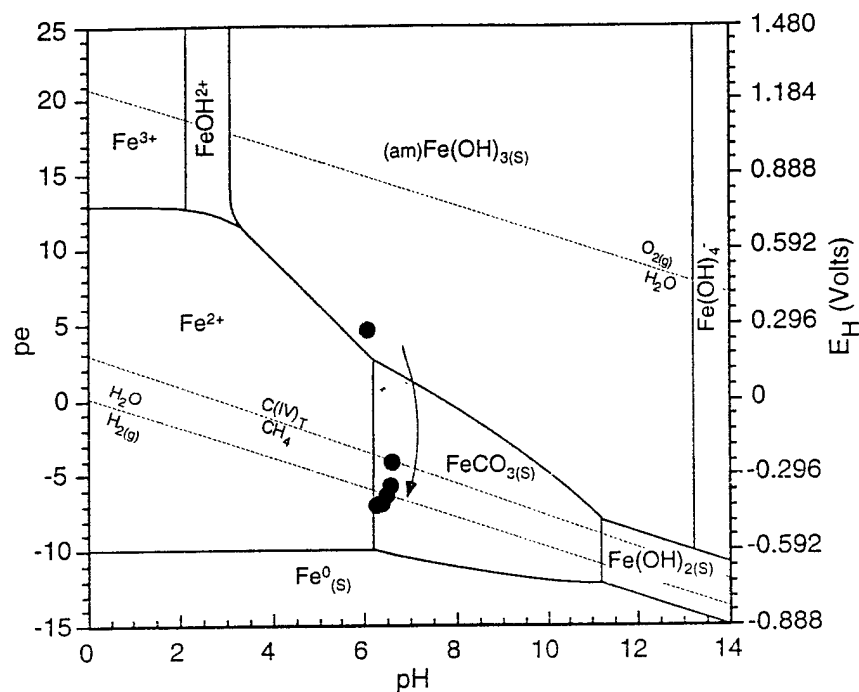


Figure 1: Stability diagram for $\text{FeCO}_3(\text{s})$, $\text{Fe}(\text{OH})_2(\text{s})$, and $\text{Fe}(\text{OH})_3(\text{s})$ formation in a $\text{Fe-H}_2\text{O-CO}_2$ system; drawn for $\text{Fe}_{\text{Total}} = 10^{-5} \text{ M}$ and $\text{C}_{\text{Total}} = 1.5 \times 10^{-2} \text{ M}$. Activity corrections neglected. Below $\text{C(IV)}_{\text{T}}/\text{CH}_4$ line, all Eh-pH lines involving FeCO_3 assume constant $\text{C}_{\text{Total}} = 1.5 \times 10^{-2} \text{ M}$ (drawn after Pankow, 1991). Slow kinetics may not allow Fe_2O_3 and Fe_3O_4 formation in model system. The data points (measured periodically for 5 days) and arrow indicate trend in Eh-pH evolution and possible $\text{FeCO}_3(\text{s})$ formation. See Fig. 3 for effect on nitro reduction kinetics during the period.

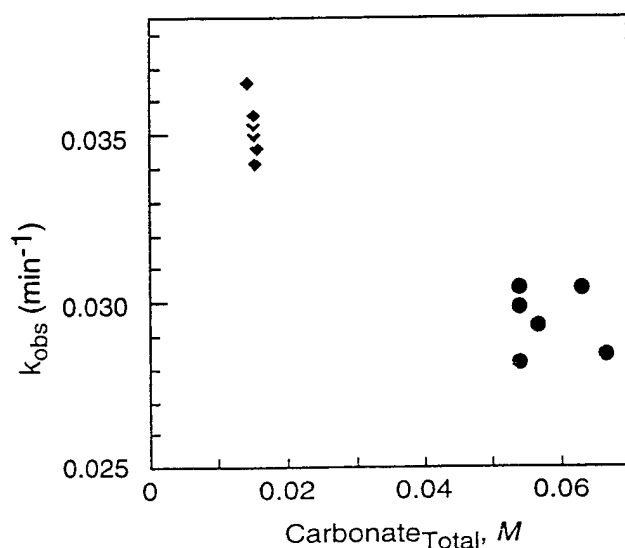


Figure 2: Effect of $[\text{HCO}_3^-]$ on the rate of nitro reduction by Fe^0 in batch systems. Decrease in Fe^0 reactivity is due to formation of FeCO_3 on the metal surface.

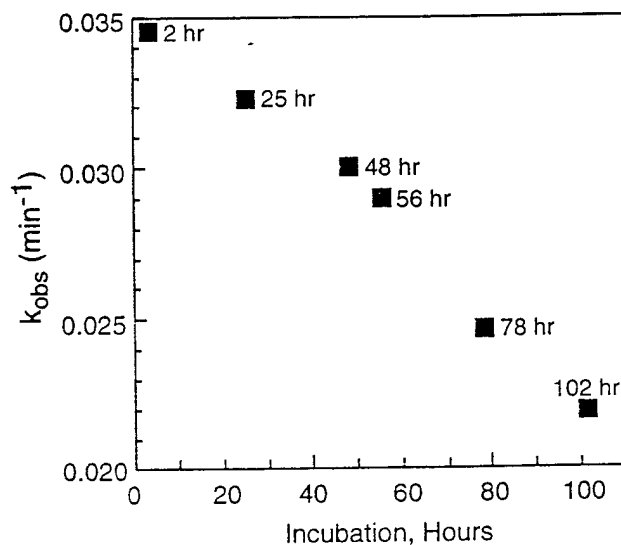


Figure 3: Gradual decline in the rate of nitro reduction by Fe^0 (following metal incubation in a bicarbonate buffer for 5 days at $\text{C}_{\text{Total}} = 1.5 \times 10^{-2} \text{ M}$). See Fig. 1 for Eh-pH variation over the experiment duration.

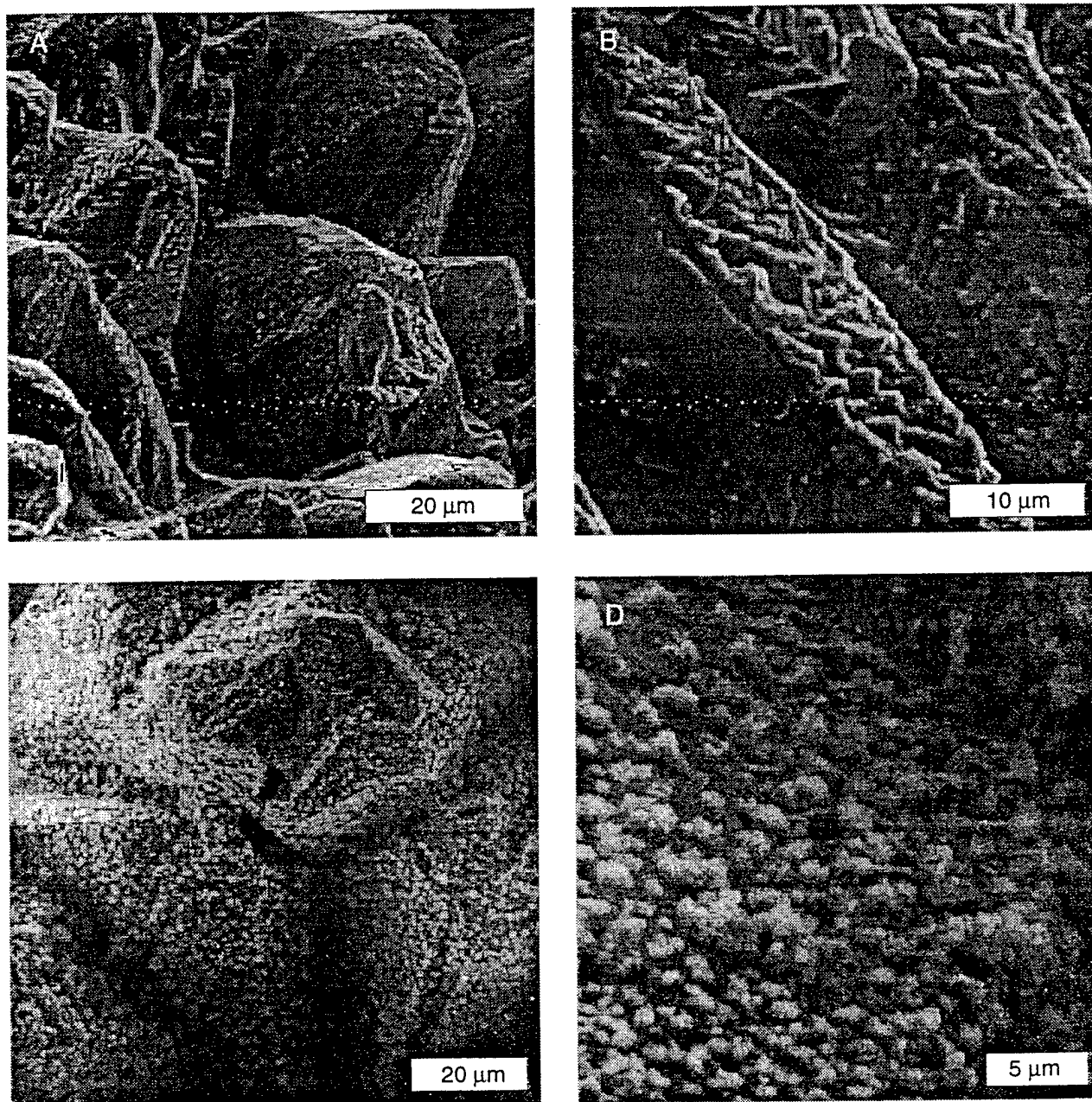


Figure 4: Scanning electron micrographs showing changes on the iron metal surface during exposure to a deoxygenated bicarbonate medium: (A) clean metal sample following washing in dilute HCl (10% v/v) prior to incubation in bicarbonate buffer; magnification: x700. (B) same sample as in 'A' at magnification: 2000x. (C) iron metal sample from 'A' exposed in bicarbonate buffer ($C_{\text{total}} = 0.1 \text{ M}$) for 18 hours; magnification: x700. (D) same sample as in 'C' at magnification: x3000. EDS analysis confirmed that the crystalline aggregates are predominantly siderite (FeCO_3).

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P. 720
- 723